

NASA Contractor Report 198425

A Porous Ceramic Interphase for SiC/Si₃N₄ Composites

Linus U.J.T. Ogbuji
NYMA, Inc.
Brook Park, Ohio

November 1995

Prepared for
Lewis Research Center
Under Contract NAS3-27186

LIBRARY COPY

DEC 12 1995

LANGLEY RESEARCH CENTER
LIBRARY NASA



National Aeronautics and
Space Administration



NF01031

A Porous Ceramic Interphase for SiC/Si₃N₄ Composites

Linus U.J.T. Ogbuji
NYMA, Inc.
2001 Aerospace Pkwy
Brookpark, OH 44142

Abstract

A suitable interphase material for non-oxide ceramic-matrix composites must be resistant to oxidation. This means it must exhibit a slow rate of oxidation, and its oxidation product must be such as to ensure that the system survives oxidation when it does occur. Because the current benchmark interphase materials, carbon and boron nitride, lack these qualities, a porous fiber coating was developed to satisfy both the mechanical and oxidative requirements of an interphase for the SiC/SiC and SiC/Si₃N₄ composites that are of interest to NASA. This report presents the interphase microstructure achieved and the resulting characteristics of fiber push-out from a matrix of reaction-bonded silicon nitride (RBSN), both as-fabricated and after substantial annealing and oxidation treatments.

Introduction

The mechanical function of the fiber-matrix interface in brittle composites is to assure load transfer from matrix to fiber, and enhance damage control through the diversion of matrix cracks away from the fiber. The diversion assures fiber debond from the matrix and hence "graceful" (as opposed to catastrophic) failure of the composite. At present, carbon (C) or boron nitride (BN) is used at the interface in developmental non-oxide ceramic-matrix composites (CMCs) because, in their turbostratic forms, these materials exhibit high compliance for load transfer, and low strength that permits fiber debond when intersected by a crack. However, C and BN pose unacceptable oxidation problems: When exposed to the atmosphere (by an open matrix crack, for instance), they oxidize rapidly. If the interface layer is thicker than $\sim 1 \mu\text{m}$ ⁽¹⁾, the oxidation leaves behind a corresponding cylindrical void around the fiber (in the case of carbon), which prevents load transfer and may act as a flaw in the composite; and if it is thin ($< 0.1 \mu\text{m}$)⁽¹⁾ the void fills up with silica from oxidizing fiber and matrix (and hence a borosilicate glass, in the case of BN), which embrittles the CMC below the glass transition temperature. These problems make it necessary to seek an alternative interfacial material that is slow to oxidize, and in a form that enhances the oxidation survival of the system.

Strictly from the stand-point of the mechanical function, a ceramic interphase with a high volume fraction of finely-dispersed porosity has been suggested as a suitable interphase material since porosity reduces shear strength and would thus permit debond by preferential fracture of the interphase⁽²⁾. Figure 1 is a schematic diagram comparing the expected locus of failure in a porous, brittle interphase with that in the case of C or BN. Porous interphase materials have been studied in oxide/oxide systems (such as in an Al₂O₃/ZrO₂/Al₂O₃ composite⁽³⁾). However, comparable studies of porous interphase materials in non-oxide CMCs (such as

silicon carbide or silicon nitride matrix reinforced with SiC fiber) are lacking. Non-oxide systems are favored over oxide systems for the applications of interest to NASA—for instance, in the hottest sections of advanced turbines—because of their superior mechanical properties at elevated temperatures. Accordingly, the aim of this project was to design a porous, ceramic interphase that fulfills the mechanical role described above, and which is suitable for SiC/SiC or SiC/Si₃N₄ composites. In this context, “suitable” refers to thermal and chemical compatibility under the envisaged aggressive service conditions, to avoid unwanted reactions with the fiber or matrix, as well as good CTE match to minimize residual stresses.

Procedure

Silicon nitride was chosen as the primary interphase material, since it exhibits the lowest oxidation rate of all silica formers. Silicon oxynitride was also considered, for the same reasons. These two materials and their oxidation product, SiO₂, are inert to the fiber (SiC) the matrix (SiC or Si₃N₄), and their oxidation product, SiO₂. Following unsuccessful efforts to make porous silicon nitride or oxynitride by the nitridation of gel or colloidal silica, and by deposition from gas phase using incorporated excess hydrogen to generate pores^(4,5), a slurry route was adopted, and it proved a very convenient means of applying the interphase as a coating on fibers. The slurry was made from 0.5μm Si₃N₄ powder, with about 20 wt% colloidal SiO₂ to bond the silicon nitride together, and 40-50 vol% polystyrene microspheres serving as fugitive templates for pores. Application on fibers involved optimizing the slurry viscosity to achieve a uniform, 1-2 μm dry coat on the fibers. For this preliminary stage of investigating the feasibility of such an interphase, the easier to handle and relatively inexpensive large diameter SiC fiber from Textron (SCS-0) was considered adequate.

Consolidation of the coating involved very slow calcination to 600°C to expel volatiles and generate porosity, followed by brief sintering in N₂ at 1350°C during which the particulate Si₃N₄ was bonded together by the minor amount of SiO₂ through interdiffusion. It was found necessary to protect the porous interphase from becoming impregnated with Si₃N₄ during reactive incorporation into a matrix. This was accomplished with an overcoat of dense silica, following which successful incorporation into reaction-bonded silicon nitride was routinely achieved. In contrast, even with the silica overcoat, attempts to reinforce reaction-formed silicon carbide (RFSC) ceramics with the coated fibers failed, owing to permeation and attack of the coating by the very reactive infiltrant of molten Si.

Assessment of system compatibility involved comparing the statistical strengths of the uncoated fibers with those of fibers recovered by removal of the coating, both after calcination and after annealing. This was to determine whether any strength-degrading reactions had occurred between fiber and coating. Uncoated fibers were also taken through the heat treatment cycles, in order to find out whether any observed strength degradation was attributable to thermal exposure alone or to reaction between the fiber and coating. For evaluating the mechanical response of the interphase, standard push-out tests were performed⁽⁶⁾. This was

done on the RBSN minicomposites as-fabricated; after annealing in N₂ for 500 hours at 1350°C; and after severe oxidation tests, in which the composites were cut into wafers and oxidized for up to 100 hours at 1200, 1300, and 1400°C. The annealing treatment was intended to assess the persistence of the porous microstructure through service at high temperatures where the high driving force for sintering might cause coarsening or loss of the porosity. The oxidation treatment was intended to simulate what might happen in service if a matrix crack exposed the interphase to atmospheric oxygen; the exposures at 1400°C were essentially accelerated tests of long-term oxidation at the lower temperatures.

Results

The design goal of the porous interphase structure is illustrated in figure 2, and the microstructure actually achieved is shown in figures 3 (coating surface) and figure 4 (cross section). Cracks form in the coating during calcination and open into fissures during annealing, leaving the coating continuous but patchy on the fiber, as figure 3(b) shows. In figure 4 the porous microstructure of the interphase may be seen to persist through the heat treatment cycles (a), and push-out testing (b). These results of the design and fabrication phase of the project have been reported at the HITEMP Review-94⁽⁶⁾, and at the 19th Cocoa Beach Conference on Composites and Advanced Ceramics⁽⁷⁾.

The results of the evaluation phase of the project are highlighted in Figs. 5-7. Figure 5 is a chart of the fiber mean strengths after various treatments. It illustrates the well-known problem that any handling of the virgin fiber degrades it (by creating surface flaws), but it shows that little *additional* degradation of fiber strength arises from the coating and/or heat treatments of the coated fiber.

Figure 6 compares the push-out performance of this interphase and that of the same fiber with a carbon coating, and with no coating at all. The figure shows that, without interfacial coating between SCS-0 fiber and RBSN matrix, push-out was not achieved at stresses up to 200 MPa (where the punch broke and the test was aborted)⁽⁸⁾; thus, a "coatingless" composite of this system would fail in a catastrophic manner. In contrast, with the porous interphase push-out was routinely achieved. The mean push-out stress for the porous interphase (50±10 MPa for debond and 30±5 MPa for sliding) is considerably higher than the 10 MPa characteristic of SCS-6 in RBSN⁽⁸⁾ (i.e., the same fiber and matrix, with a carbon interface). Figure 7 compares the push-out performance of the porous interphase system as-fabricated, and after various thermal and environmental exposures.

Discussion

Figure 5 shows that the strength degradation of coated fibers is comparable to that observed in uncoated fibers. It may be attributed to handling, rather than to any reaction between fiber and coating, or between coating and matrix. Compatibility of the fiber coating is not an issue in this system.

Compared with SCS-0 in RBSN, the porous, brittle interphase is definitely a large improvement over the coatingless system. On the other hand, it is not clear whether the porous, brittle interphase is a significant improvement over that of a carbon interface (SCS-6 in RBSN) in terms of mechanical response. In both cases fiber debond and sliding are achieved. The higher push-out stress in the former case implies that more energy is needed for a crack to propagate through the porous interphase than through a carbon interface, and this may be an advantage of the porous interphase. If so, this gain is incidental.

The main advantages of the porous interphase lie in protection against oxidation. Firstly, the oxidation rate of the silicon nitride interphase is slower, by orders of magnitude, than the rate of consumption of a carbon interface by oxidation. Secondly, the consequences of oxidation seem to be mitigated by porosity. As figure 7 shows, the push-out characteristics are not significantly impaired by either severe oxidation or prolonged annealing: the debond and sliding stresses stay within the current envelope defined, for the same fiber and matrix, by a coatingless system (SCS-0 in RBSN) on one hand, and a carbon interface (SCS-6 in RBSN) on the other. After the most severe oxidation treatments (100 hours at 1200 to 1400°C), the interphase and its adjacent shells of fiber and matrix have probably been fully converted to silica; nevertheless, push-out still occurs. It is likely that the interphase stayed porous after oxidation, and so remained the preferred path for crack propagation. In this respect, the present system is both an oxidation resistant and oxidation surviving system.

The pores and fissures in the interphase serve an additional, positive role. The oxidation of silicon carbide or nitride to silica results in large volumetric increase, which can set up residual stresses in systems where dense silica fills up the space between fiber and matrix. In the present system, however, the interphase fissures and voids are expected to act as a sink for the excess volume generated by oxidation of the CMC components, the interphase is sufficiently porous to absorb the excess volume.

A deleterious effect of the porosity and fissure is that they allow permeation and attack of the interphase by aggressive process fluids. Hence all efforts so far to incorporate coated fibers into RFSC have failed. Even when the interphase was sealed with a dense layer of silica, the coating was consumed and the fiber was extensively attacked by the molten silicon.

Conclusion

A slurry-based fiber coating, made of silicon nitride and silica, has been found to generate a porous interphase, which exhibits the desired characteristics in SiC/Si₃N₄ composite systems. The interfacial properties survived the rigorous conditions of processing, prolonged post-annealing, and severe post-oxidation treatments.

Future Work

1. Preliminary trials have shown that adding submicron carbon powder to the slurry drastically reduced the sort of cracking shown in figure 3(a). However, the resulting slurry needed to be thinned to viscosities in the narrow range of 7-10 mPa-s in order to achieve uniform coating of the SCS0 fiber. (This may be compared to the 70-100 mPa-s needed for the coatings shown in figures 3 and 4.) At such low viscosities, achievable coating thickness was inadequate for microstructural study of the sort shown in figure 4. Future work will be aimed at optimizing the viscosity and particle loading of the slurry to produce carbon-containing coatings which will not crack, and which will survive incorporation in RFSC matrix.
2. In preliminary efforts to apply this interphase coating on the small-diameter fibers of Hi-NicalonTM tows, fibers in the interior were inadequately coated, because of poor permeation of the tow envelope. This is a general problem in the application of slurry coatings to fiber tows and weaves. Future work will seek to optimize slurry viscosity and composition (as mentioned above) to improve permeation of tows. More important, attention will be paid to devising a new way (other than passive dipping) to apply the slurry on small-diameter fibers. One approach to be pursued involves jet injection of the slurry into tows and weaves.
3. In a collaborative effort now underway, porous ceramic interphase coatings will be deposited from the chemical vapors (using an excess of fugitive carbon to generate porosity), and characterized in the manner described in this report.

References

1. L. Fillipuzzi, G. Camus, and R. Naslain, "Oxidation Mechanism and Kinetics of 1D-SiC/C/SiC Composites", J. American Ceramic Society, 77 [2] (1994) 459-66.
2. H. Carpenter and J. Bohlen, "Fiber Coatings for Ceramic Matrix Composites", pp. 238-256 in Ceramic Engineering & Science Proc., Jul-Aug. 1992, ed. J. Wachtman, American ceramic Society, Westerville, Ohio.
3. J.B. Davis, J.P. Lofvander, and A.G. Evans, "Fiber Coating Concepts for Brittle-Matrix Composites", J. American Ceramic Society, 76 [5] (1993) 1249-57.
4. L. Ogbuji and D.R. Harding, Determining the Biaxial Strength of PECVD Silicon (Oxy)Nitride Films", Elevated Temperature Coatings: I, Science & Technology, ed. N.B. Dahotre, J.M. Hampikian, and J.I. Stiglich, TMS, Warrendale, PA, 1994.

5. L.U. Ogbuji, "Porous Si-O-N Coatings for CMC Interfaces"; pp. 80-1 to 80-19 in HITEMP Review 1994, NASA Research Conference Publication 10146, Cleveland, OH 1994.
6. J.I. Eldridge, "Desktop Fiber Push-out Apparatus", NASA Tech. Memo. #105341, Dec. 1991.
7. L. U Ogbuji, "A Porous, Oxidation-Resistant Fiber Coating for CMC Interphase", Proc. 19th Ann. Conf. On Composites, Advanced Ceramics, Materials, and Structures, Cocoa Beach, FL 1994.
8. J.I. Eldridge and R. Bhatt, "Experimental Investigation of Interface Properties in SiC Fiber-Reinforced Reaction-Bonded Silicon Nitride Matrix Composites"; Proc. MRS 1994.

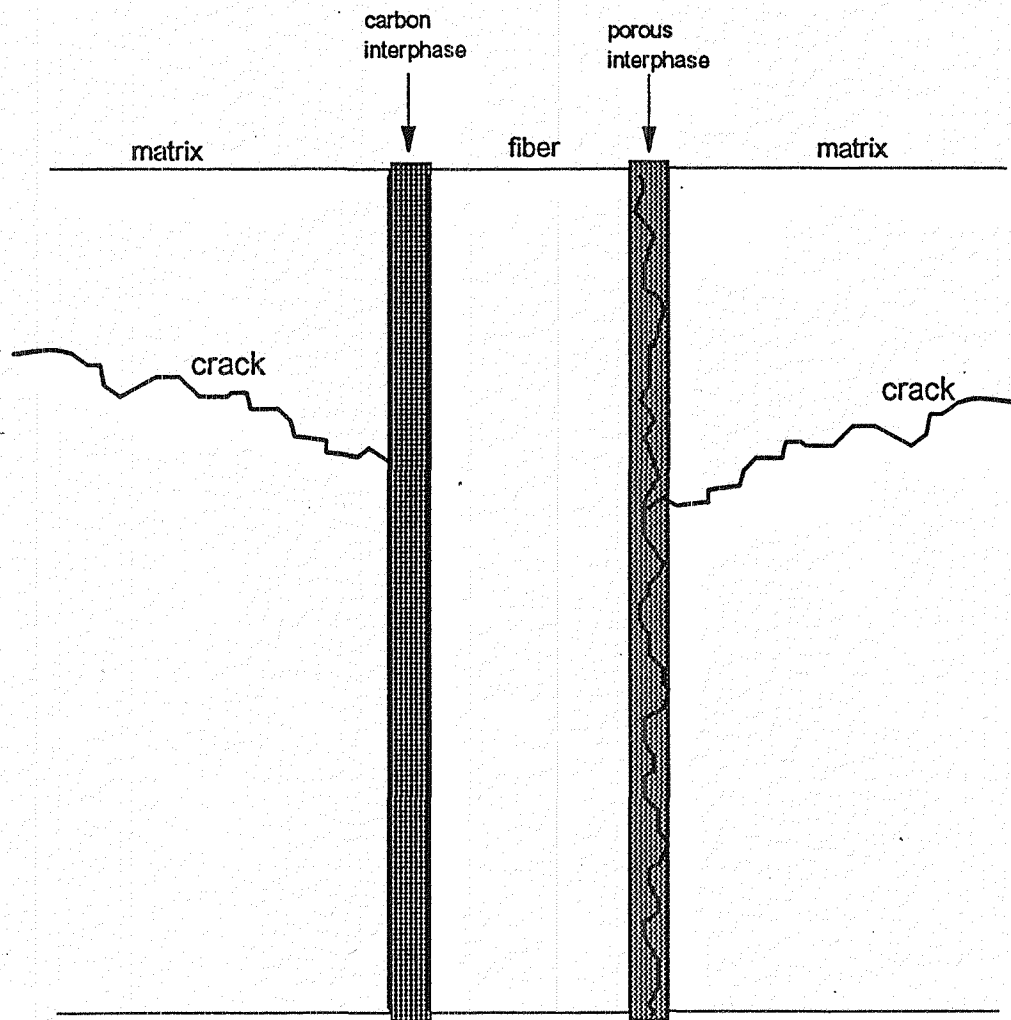


Fig. 1, Schematic diagram illustrating crack diversion at a CMC interphase: interfacial debond at a carbon (or BN) interface, and bulk fracture in a porous interphase.

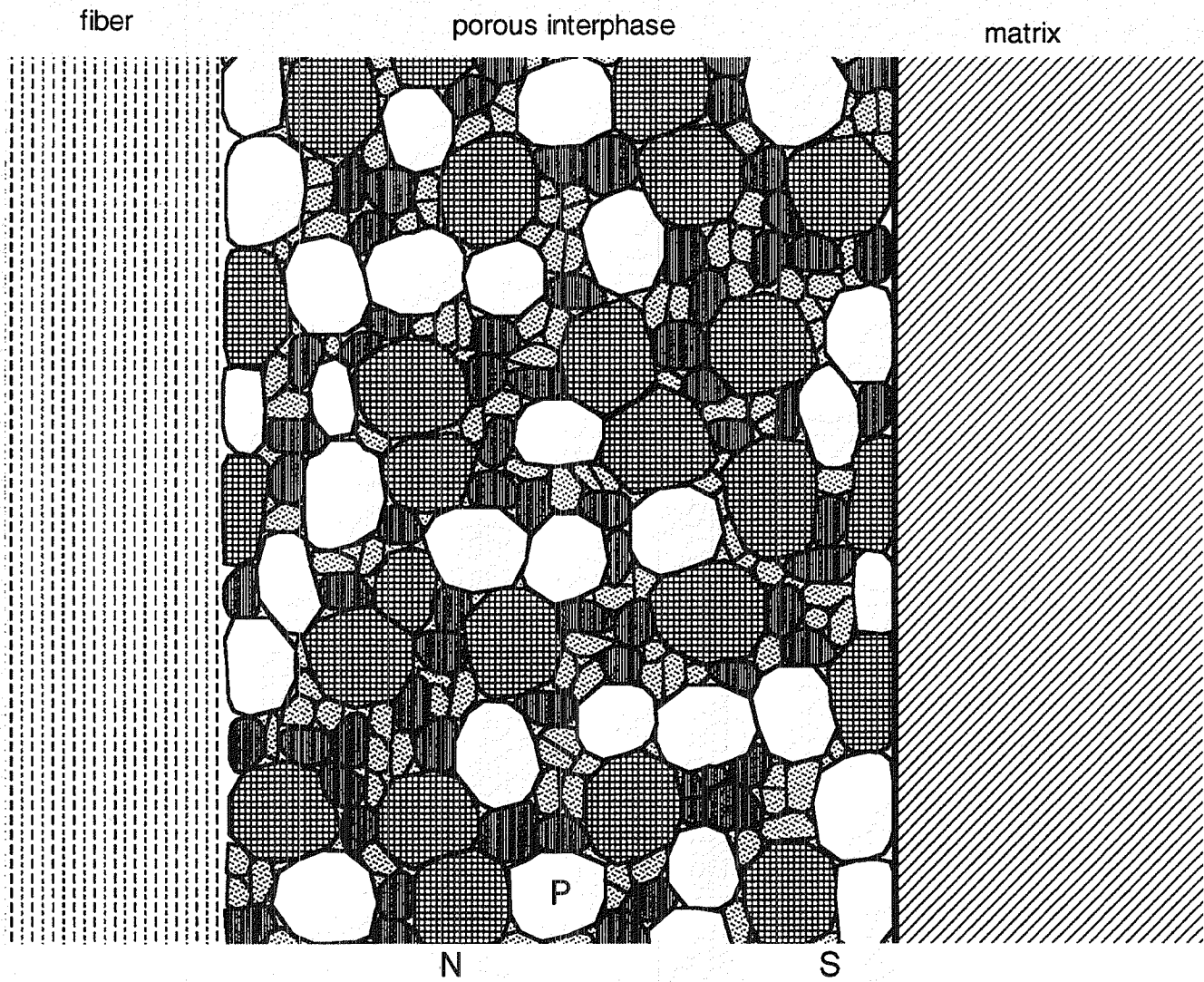
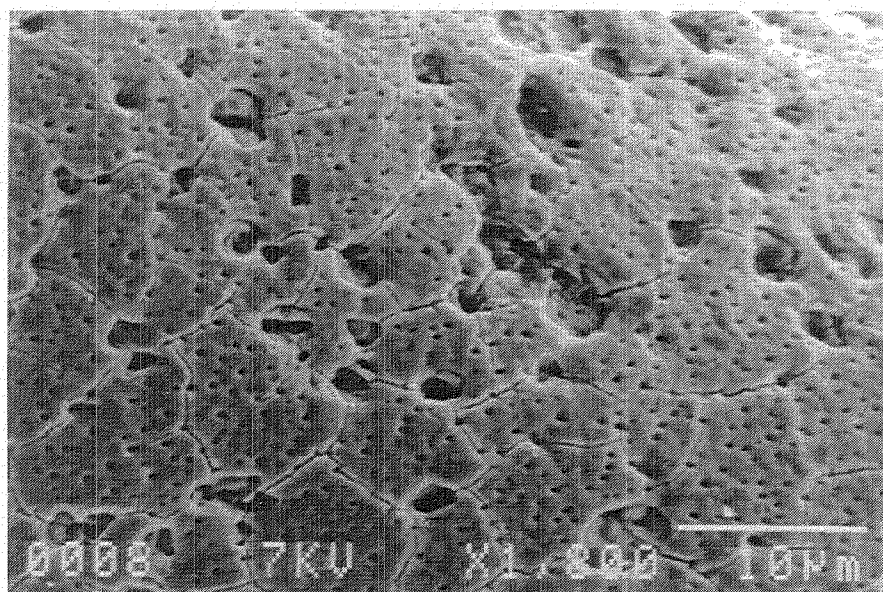
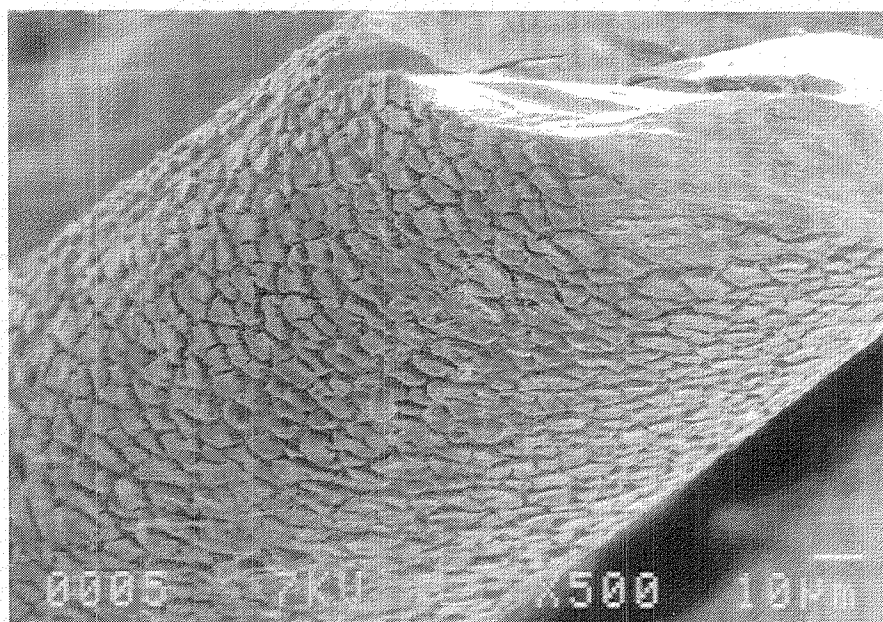


Fig. 2, Schematic illustration of desired microstructure: silicon nitride, N, is the main component, P is porosity, and S is silica (minor phase) for cementation.

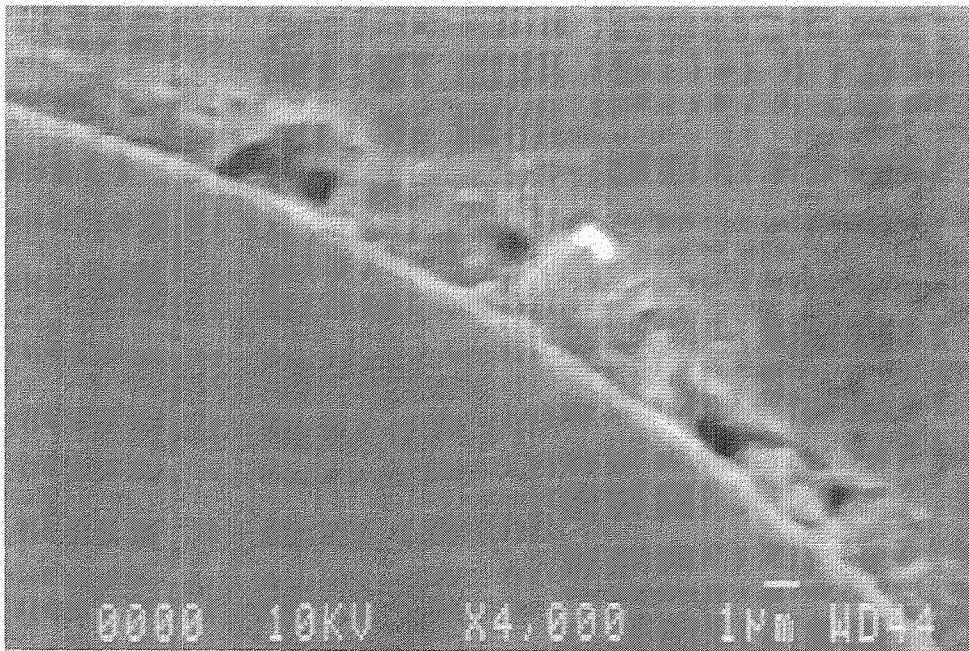


(a)

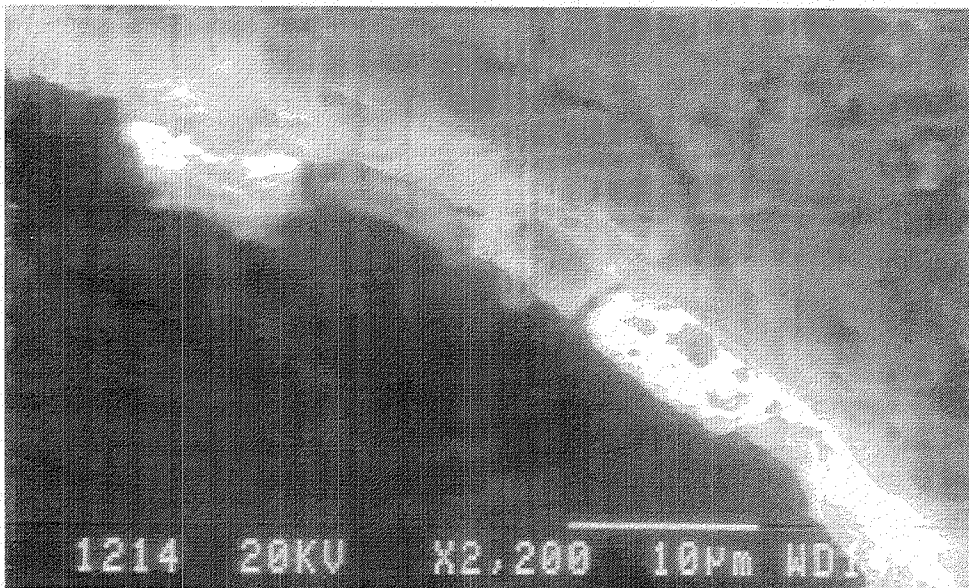


(b)

Fig. 3, SEM micrographs of the coating surface showing cracks that develop during calcination (a) and widen during annealing (b), rendering the coating coverage patchy.



(a)



(b)

Fig. 4, SEM micrographs showing cross-sections of minicomposite (a) before, and (b) after fiber push-out. Interphase porosity is evident in both cases.

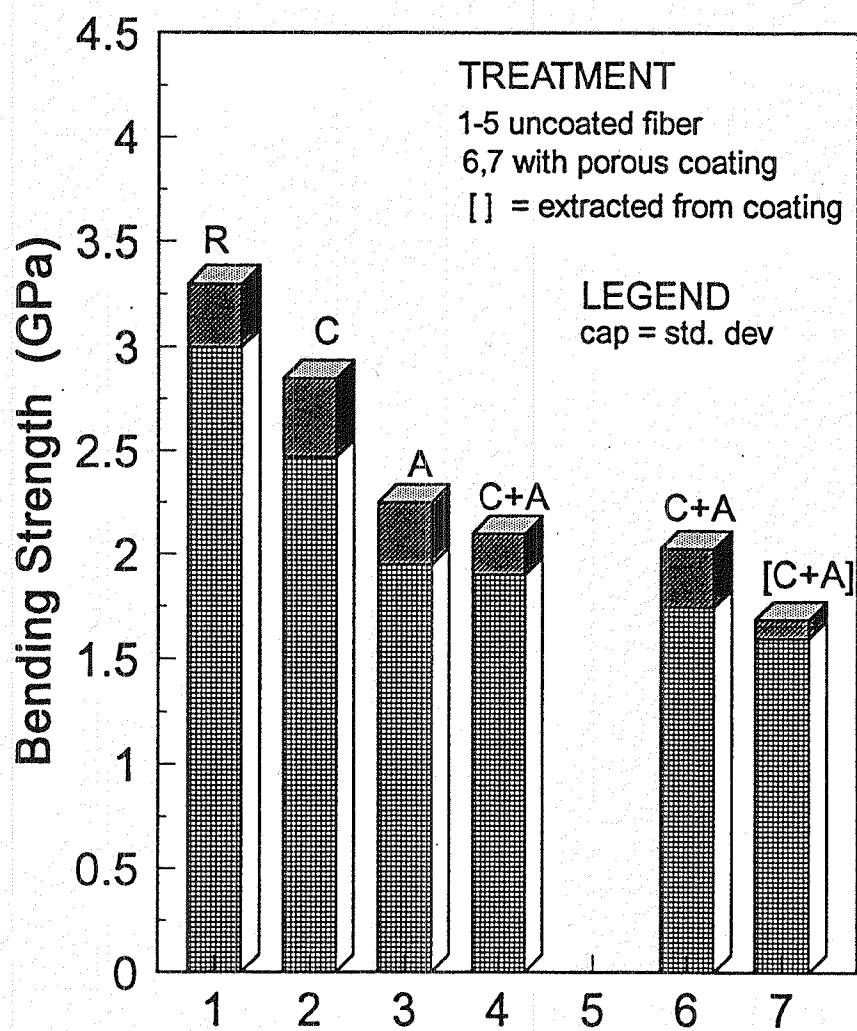


Fig. 5, Bending strengths of SCS-0 fibers after treatment as indicated: R, as received; C, calcined; A, annealed. # 6 fibers were tested with porous coating on; #7 after removing the coating with HF.

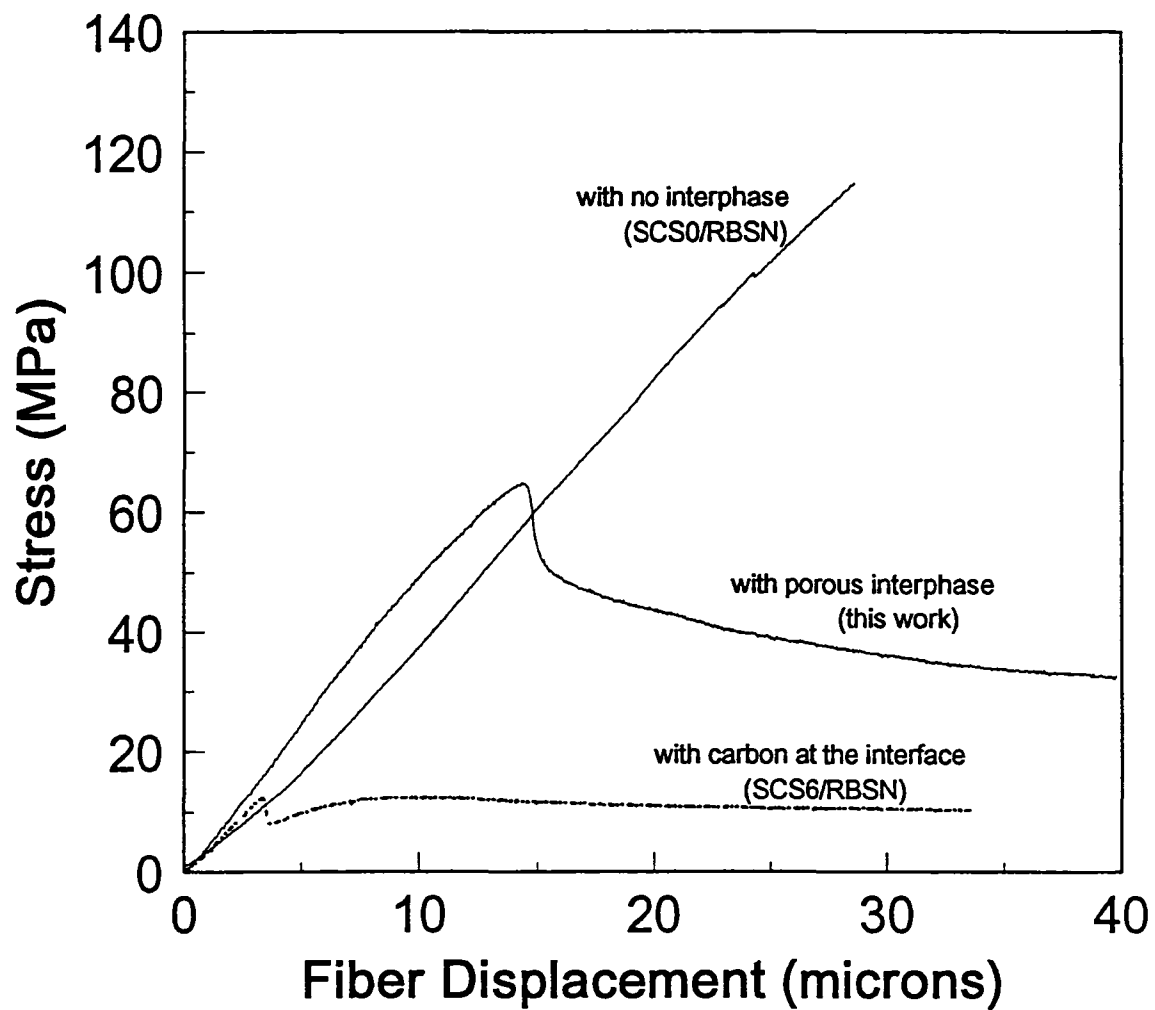


Fig. 6, Fiber push-out behavior for Textron's CVD SiC fiber in RBSN matrix, with a porous interphase, with no interphase, and with carbon at the interface

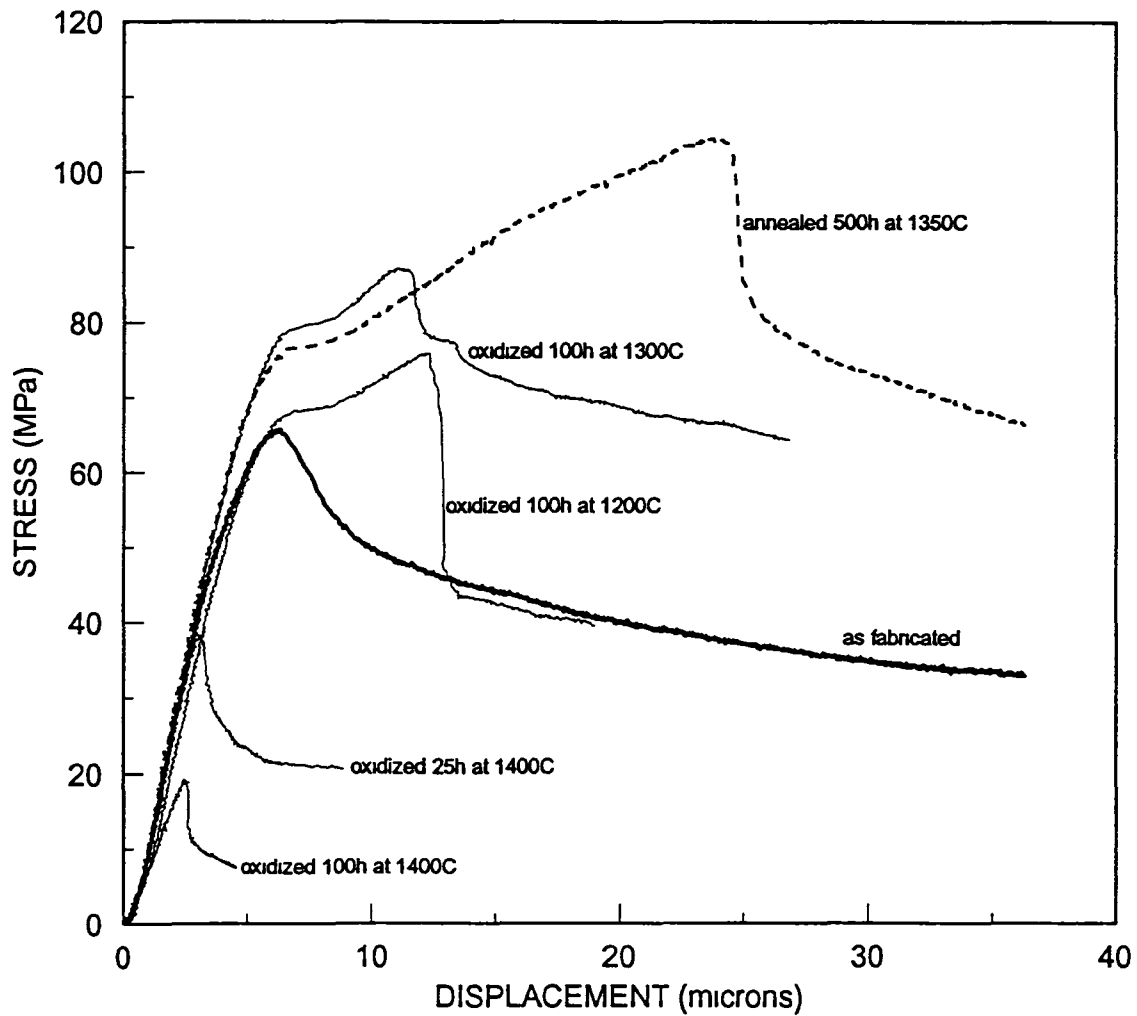


Fig.7, Effect of oxidation and annealing on the fiber push-out behavior of SCS/RBSN minicomposites made with the porous interphase.

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 1995	3. REPORT TYPE AND DATES COVERED Final Contractor Report		
4. TITLE AND SUBTITLE A Porous Ceramic Interphase for SiC/Si ₃ N ₄ Composites		5. FUNDING NUMBERS WU-505-63-12 C-NAS3-27186		
6. AUTHOR(S) Linus U.J.T. Ogbuji				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NYMA, Inc. 2001 Aerospace Parkway Brook Park, Ohio 44142		8. PERFORMING ORGANIZATION REPORT NUMBER E-10013		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA CR-198425		
11. SUPPLEMENTARY NOTES Project Manager, Leslie Greenbauer-Seng, Materials Division, NASA Lewis Research Center, organization code 5160, (216) 433-6781				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category 27 This publication is available from the NASA Center for Aerospace Information, (301) 621-0390			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A suitable interphase material for non-oxide ceramic-matrix composites must be resistant to oxidation. This means it must exhibit a slow rate of oxidation, and its oxidation product must be such as to ensure that the system survives oxidation when it does occur. Because the current benchmark interphase materials, carbon and boron nitride, lack these qualities, a porous fiber coating was developed to satisfy both the mechanical and oxidative requirements of an interphase for the SiC/SiC and SiC/Si ₃ N ₄ composites that are of interest to NASA. This report presents the interphase microstructure achieved and the resulting characteristics of fiber push-out from a matrix of reaction-bonded silicon nitride (RBSN), both as-fabricated and after substantial annealing and oxidation treatments.				
14. SUBJECT TERMS Porous; Ceramic; Interphase, Coating; Environmental tests; Push-out stresses			15. NUMBER OF PAGES 15	
			16. PRICE CODE A03	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	